TRANSACTIONS, ILL. STATE ACAD. SCI.
Vol. 68, No. 2 (1975)

A COMPUTER SIMULATION OF LIQUID NEON AT 35° K

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Abstract--The radial distribution function (RDF) and pressure of liquid Ne^{20} were the objectives of a computer simulation using the method of molecular dynamics. Modifications of purely classical simulations were introduced in order to correct for the semi-classical behavior of the fluid. While computed results indicate good agreement for the radial distribution function, the calculated pressures demonstrated the sensitivity of this property to very specific details of the pair potential function.

INTRODUCTION

We report results of computer experiments on a system of 500 particles interacting by a Lennard-Jones 6-12 potential under conditions which represent the Ne^{20} isotope at 35°K and a density corresponding to the liquid in equilibrium with its vapor. While computer studies have been published for argon (Rahman, 1964; Verlet, 1967, 1968), there appear to be none for neon. This is in part due to the nature of the Lennard-Jones potential when expressed in dimensionless variables: specific molecular parameters no longer appear in the energy or force relationships, thus implying corresponding states in terms of reduced temperature and density. There are differences with Ne, however, as the thermal de Broglie wavelength of atoms at 35° K suggest the possibility for quantum effects. Furthermore, this study corresponds to conditions for which reliable neutron scattering data is available (de Graaf and Mozer, 1971), while there have been no reports of a computer experiment on Ar under the same reduced conditions.

The present work uses the method of molecular dynamics to obtain the Ne RDF. Pressure is then calculated from the RDF by use of the virial theorem (Hirschfelder et al., 1954, p. 134). Quantum effects may arise from three sources: exchange (identical particles), diffraction, and zero point motion. Exchange forces have been shown to be insignificant at the temperatures and density of this study (Jaen and Khan, 1967); furthermore, diffraction effects are significant only when the thermal de Broglie wavelength,

$$\lambda = h/(2mk_BT)^{\frac{1}{2}} \qquad (1)$$

is comparable in magnitude to atomic dimensions (Hirschfelder et al., 1954, p. 413). h in the equation is Planck's constant (6.62×10^{-27} erg-sec), m is the particle mass in grams, k_B is Boltzmann's constant, and T is the Kelvin temperature. Since, $\lambda = 0.19$ Å for Ne at 35° K, while its atomic "diameter" is 2.75 Å, diffraction effects are also not a major consideration. Zero point motion may be determined by means of Wigner's analysis of a semi-classical system (Landau and Lifschitz, 1958, pp. 96-103). He showed that, to order h^2, the momentum distribution of a semi-classical system remains Maxwellan,

$$dn(p) = (\text{const})\exp(-p^2/2mk_BT_{eff})4\pi p^2 dp \qquad (2)$$

provided that the thermodynamic temperature is replaced by an "effective temperature",

$$T_{eff} = T + \frac{m\,h^2 \langle a^2 \rangle}{36 k_B{}^3 T^2} \qquad (3)$$

$\langle a^2 \rangle$ is the mean square acceleration for the classical system,

$$\langle a^2 \rangle = \frac{1}{N} \sum_{i=i}^{N} (\vec{a}_i \cdot \vec{a}_i) \qquad (4)$$

The difference, $T_{eff} - T$, amounts to about 5 degrees in Ne at 35° K. Zero point motion thus appears to be the most significant effect. To account for this, two computer runs are presented: one entirely classical at 35° K, and a second at a higher temperature (41.2° K) which has a momentum distribution corresponding to that given by equations (2) and (3). The increase in average speed of particles of the system also changes trajectories, although not entirely in a manner which would correspond to that predicted by a semi-classical analysis of scattering.

Another consideration is the change of pair potential due to the low temperature. There are several approaches to this problem, the most straightforward being that of Deutch et al. (1966), who presented a semi-classical pair potential in the simple form:

$$U_{sc} = U_{cl} + \frac{\lambda^2}{6} \nabla^2 U_{cl} \qquad (5)$$

where U_{sc} is the semi-classical pair potential and U_{cl} is the classical Lennard-Jones potential. λ is again the thermal de Broglie wavelength. It will be seen that such a consideration, while not large in determining the radial distribution function, can be very important in properties related directly to the force law derived from eq. (5).

METHOD

Detailed descriptions of the methods used for computation are contained in articles by Rahman (1964), Verlet (1967), and the thesis of Chen (1974). Essentially, the method of molecular dynamics involves computation of the total force, $\vec{F}_i$, acting upon a particle, i, due to other particles in the system. Then, using Newton's law,

$$\vec{a}_i = \vec{F}_i/m \tag{6}$$

the acceleration of the particle is numerically integrated, by which its trajectory can be determined. This is done for each particle in the system over a series of steps which correspond to the time evolution of particle motion. The force is derived from the Lennard-Jones potential

$$U_{ij} = 4\epsilon\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right] \tag{7}$$

where r_{ij} is the magnitude of the distance from the i^{th} to the j^{th} particle. The x-component of force in eq. (6) is then

$$F_{xi} = 24\epsilon \sum_{\substack{j=1,N \\ j\neq i}} \frac{x_{ij}}{r_{ij}^{2}}\left[2(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right] \tag{8}$$

σ and ϵ are for Ne 2.75 Å and 4.9×10^{-15} ergs, respectively. Similar expressions are obtained for the y- and z-components. Integration of eq. (6) is accomplished by the formula of Verlet (1967), which gives the position of a particle at time $t+\Delta t$, knowing its position at times t and $t-\Delta t$:

$$x_i(t+\Delta t) = -x_i(t-\Delta t) + 2x_i(t) + a_{xi}(t)\ \Delta t^2 \tag{9}$$

The velocity at time t is then

$$v_{xi}(t) = \frac{x_i(t+\Delta t) - x_i(t-\Delta t)}{2\,\Delta t} \tag{10}$$

Temperature can be obtained by the mean square momentum derived from the distribution of eq. (2):

$$\left\langle p^2 \right\rangle /2m = \frac{1}{N}\sum_i(\vec{p}_i\cdot\vec{p}_i) = \frac{1}{N}\sum_i m(\vec{v}_i\cdot\vec{v}_i)$$

$$= \frac{1}{N}\int p^2 dn(p) = 3/2\ k_B\ T_{eff} \tag{11}$$

Thus,

$$T_{eff} = \left\langle p^2 \right\rangle /3mk_B \qquad (12)$$

Since the calculation of the interactions between every pair of 500 particles is very lengthy, computation was restricted to pairs of particles with distances equal to or less than 2.5σ. Interactions at greater distances have been shown to be negligible (Verlet, 1967). For convenience, reduced dimensions were employed by taking σ as a unit of length, ϵ as a unit of energy, and $\sigma\sqrt{\frac{m}{\epsilon}}$ as a unit of time. The computer algorithm then involved locating x, y, and z coordinates for 500 particles at positions on a face-centered cubic lattice in a cell of length 9.133σ = 25.116 Å, which corresponds to a density of 1.0624 g/cm^3. The atoms were given random displacements corresponding to a Gaussian velocity distribution with mean square of about 35° K. Using eq. (10), the coordinates were moved for about 450 steps of $\Delta t = 10^{-14}$ sec. The temperature of the system was monitored and adjusted by multiplying velocities with a corrective factor at each 20th step. After the program had run for some time (about 7 hours on an IBM 360/50 computer), the system was considered to be "equilibrated", and the next 400 steps were followed without further velocity adjustment. Positions and velocities were recorded on magnetic tape and calculations of the radial distribution fuction obtained from them. The radial distribution function is defined as the ratio of the bulk density, ρ_{bulk}, to the average microscopic local density, $\rho_i(r)$, at a distance r:

$$g(r) = \frac{1}{N}\sum_{i=i}^{N}\frac{\rho_i(r)}{\rho_{bulk}} \qquad (13)$$

This average is taken over all particles in the system, and then over a large number of configurations in time. If there are $n_i(r)$ particles which are situated at a distance between $r - \Delta r/2$ and $r + \Delta r/2$ from a particle, i, $\rho_i(r)$ is then

$$\rho_i(r) = n_i(r) /4\pi r^2 \Delta r \qquad (14)$$

From a knowledge of g(r), other equilibrium properties may be determined. The pressure, for instance, is given by

$$P = k_B T + \frac{1}{6}\rho^2 \int_0^\infty r\,\frac{dU(r)}{dr}\,g(r) 4\pi r^2 dr \qquad (15)$$

RESULTS

The temperature and total energy for the two computer runs were monitored during their progress. Averages and their standard deviations are summarized in table I.

TABLE I - Averages Determined from the Dynamics of the Computer Runs

Average Classical Temperature, $^{\circ}$K (eq. 12)	34.8	41.2
Standard Deviation, $^{\circ}$K	0.5	0.6
Semi-Classical Temperature (eq. 3)	---	37.0
Average Energy per Particle, Units of ϵ	-2.80	-2.52
Standard Deviation of Energy, Units of ϵ	2.2×10^{-3}	6.4×10^{-3}
Mean Square Acceleration per Particle, Units of $\left(\frac{\epsilon}{m\sigma}\right)^2$	515.	516.

The temperature for the run at 41.2° K was determined iteratively from values of the mean square acceleration at early states of the run by eq. (3). This overestimated the T_{eff} necessary to yield a thermodynamic temperature of 35°. However, values of the reduced acceleration and total potential energy are nearly identical for the two runs, as inspection of the radial distribution functions also suggests. Density is obviously a more significant factor in determining these quantities than the slightly different trajectories of the 41.2° run, a fact which has been previously demonstrated (Reed and Gubbins, 1973, p. 249). Radial distribution functions for the two runs are shown in figures 1 and 2, and are to be compared with the radial distribution function obtained from the neutron scattering data of de Graaf and Mozer (1971), figure 3. Inspection of the curves (table II)* reveals that the principal differences between the computer runs and the neutron scattering RDF are in the positions of the first maximum, the value for neutron scattering being at a slightly larger (0.10 ± 0.05 Å) distance. In general all three RDF's are very similar, with the major differences being substructural "disturbances" in the principal oscillations.

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* The authors will supply detailed (0.05 Å) tables of g(r) upon request.

Radial Distribution Functions Determined From Computer And Neutron Scattering Experiments

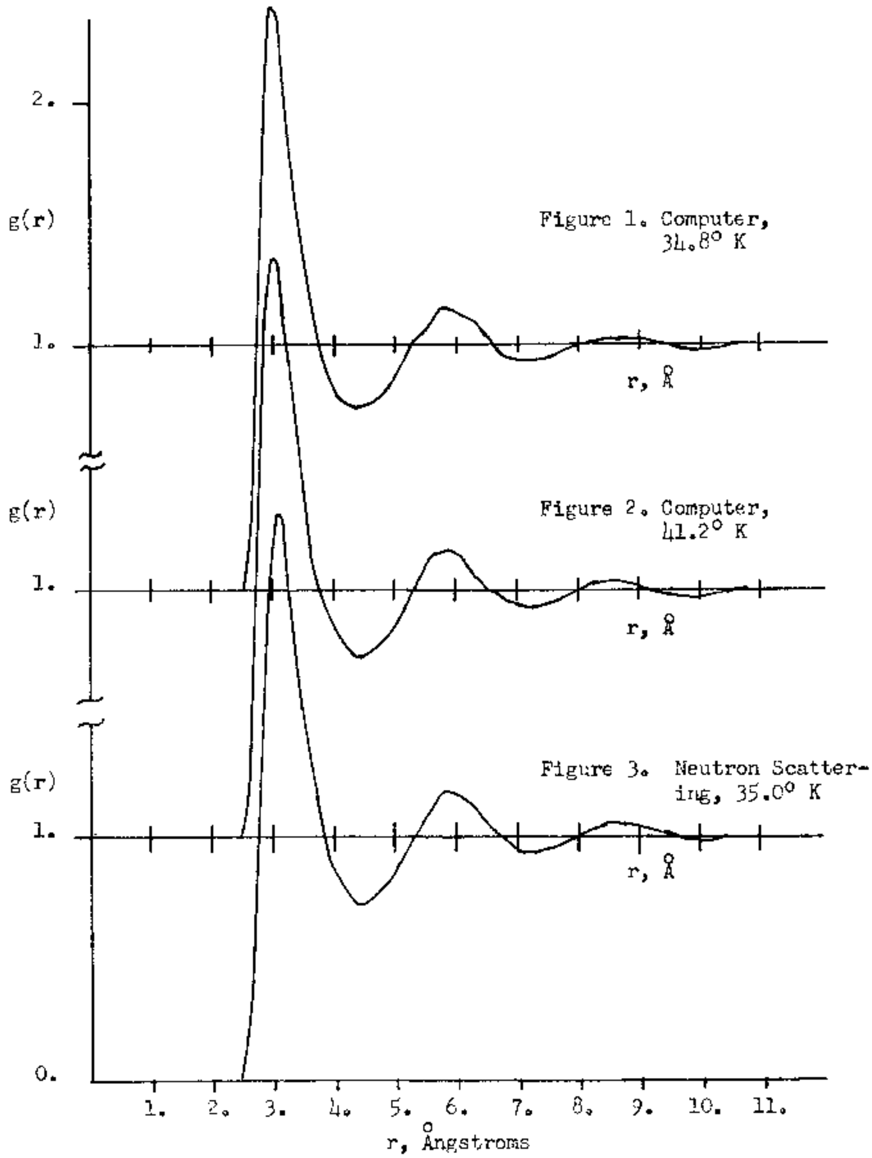

TABLE II - A Comparison of Radial Distribution Functions for Neon Determined from Computer and Neutron Scattering Experiments

	Computer, 34.8° K	Computer, 41.2° K	Neutron Scattering, 35° K (de Graaf and Mozer, 1971)
First Maximum, Å	3.00 ± 0.05	3.00 ± 0.05	3.10 ± 0.05
$g(r_{max})$	2.35	2.38	2.31
First Minimum, Å	4.55	4.50	4.45
$g(r_{min})$	0.75	0.72	0.71
Second Maximum, Å	5.80	5.85	5.85
$g(r_{max})$	1.16	1.16	1.17

Considering that random fluctuations in a time-averaged property are proportional to the inverse square root of the number of measurements, we estimate these, by comparison with the work of Verlet (1967), to be about 1.7% in g(r) for the computer runs. There is a current controversy as to whether such small substructural features in g(r) correspond to real configurational substructure in the liquid or are the result of experimental uncertainties (Fehder, 1970; Tsien and Valleau, 1974). The computer experiments presented here do not resolve that question, but it is to be noted that the initial configuration for the 41.2° computer run was one of the latter configurations of the 34.8° run. Thus with a common point in phase space, the time evolution of the two runs results in different substructural features in their radial distribution functions. RDF's derived from different portions of the two computer runs indicate that the substructural differences persist over an appreciable period of time (compared to the total run time). Much longer runs would be needed, though, before the issue could be definitely settled.

Pressures calculated from eq. (15) for the various computer runs and the g(r) derived from neutron scattering are presented in table III, using both the classical Lennard-Jones pair potential, eq. (7), and the semiclassical pair potential, eq. (5). The wide range of results indicates the sensitivity of this property to details of the computation. De Graaf and Mozer (1971) report the experimental value of $P/\rho k_B T$ to be 0.142 at 35° K.

Table III - $P/\rho k_B T$ Calculated from the Radial Distribution Functions by eq. (15).

	Computer, 34.8° K	Computer, 41.2° K	Neutron Scattering, 35° K (de Graaf and Mozer, 1971)
Classical U(r), eq. (7)	-0.44	-0.12	-0.36
Semi-Classical U(r), eq. (5)	---	0.64	0.49

DISCUSSION

Negative pressures, calculated from eq. (15) suggest in molecular dynamics calculations the possibility of a phase separation (see also Riess, 1950), a phenomenon not identical to the real event in nature because of the periodic boundary conditions. For neon, the freezing point under its own vapor pressure is 34.5° K, and such a result would not be surprising. There are possibilities other than a phase transition which could account for this effect in neon, however, specifically neglect of quantum mechanical factors. Indeed, the large positive pressure obtained from the neutron scattering RDF using the semi-classical potential function suggests that this is likely the case, even though eq. (5) may not be adequate.

In general, the effect of a semi-classical pair potential upon g(r) can be understood by examining the parameters ϵ and σ in the Lennard-Jones equation. The result of quantum behavior is to shift ϵ to smaller and σ to larger values in the semi-classical function from the classical potential. Studies upon the effects of density on g(r) (Fehder, 1970; Verlet, 1968) indicate that the principal maximum depends mainly upon the component of repulsive force which is related to σ. A larger σ would likely move the g(r) in the direction of the neutron scattering g(r). This would also have a significant contribution to the pressure virial, eq. (15). The smaller ϵ, which characterizes a smaller attractive force, would affect the subsequent principal structure. Thus, it appears that a somewhat more precise semi-classical potential function, used for the computation of particle trajectories by eq. (9), could account for the differences in the principal maximum of g(r) as well as give better results for the pressure calculated from eq. (15).

It would also be of interest to examine the microscopic transport and time dependent correlations in the fluid using an effective temperature and a semi-classical pair potential. This would help decide whether such an approach does represent the state of affairs in a real fluid under moderate conditions of temperature and pressure.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. Kup Tcheng and the Office of Institutional Research and Computer Operations at Illinois State University for making available the computer time needed in this project.

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